DESCRIPTION

Non-aqueous electrolyte secondary battery

TECHNICAL FIELD

5   The present invention relates to a non-aqueous electrolyte secondary battery.

BACKGROUND ART

10   In recent years, in order to meet the demand for ever smaller, more functional portable devices, studies on further improving the energy density of the secondary batteries to be installed on such devices have been conducted vigorously.

A lithium-ion secondary battery having a lithium transition
15   metal oxide positive electrode and a graphitic carbon negative electrode can be a typical example of high energy density secondary batteries. And, aiming for the realization of much higher energy density, the use of metal materials such as Al, Sn and Si, capable of alloying with Li, as a negative electrode is being considered.

20   However, these materials suffer significant changes in volume due to alloying; hence, the secondary batteries using these materials as a negative electrode are poor in cycle performance and insufficient for practical use. Some proposals for solving these problems have been made: for example, the use of an alloy consisting of Sn and Ni, the
25   former is capable of alloying with Li and the latter is not (e.g. Japanese Provisional Publications No. 143700 of 2001 and No. 162823 of 1998.) These proposals are designed to achieve a secondary battery with high energy density and excellent cycle performance by using the properties of Sn and Ni, that is, Sn for the attainment of high energy density and
30   Ni, which does not alloy with Li, for the maintenance of the framework structure of alloy and for the prevention of alloy degradation due to volume change.

The inventor of the present invention, too, has conducted studies on a negative electrode which is capable of achieving high
35   energy density by the use of Sn. And, as a result, he has found that it is impossible to attain sufficient cycle performance only by mixing Sn and

Ni and perform reversible charge/discharge by using a complete alloy of Sn and Ni, for example, Sn_4Ni_3 alloy, and that when an alloy having Sn phase and Sn_4Ni_3 phase is used, it is possible to realize satisfactory cycle performance and high energy density.

5   It is an object of the present invention to provide a non-aqueous electrolyte secondary battery having high energy density and satisfactory cycle performance by using an alloy comprising Ni and Sn as a negative active material.

DISCLOSURE OF THE INVENTION

10   The present invention provides a non-aqueous electrolyte secondary battery comprising a negative electrode with a composite layer containing a negative active material, a positive electrode, and a non-aqueous electrolyte; characterized in that said negative active

15   material is an alloy containing 5 to 25 mass% of nickel and 75 to 95 mass% of tin, and that such alloy contains Sn_4Ni_3 phase and Sn phase.

According to the present invention, both high energy density and satisfactory cycle performance can be provided.

It is preferable that the ratio of Sn_4Ni_3 phase and Sn phase in

20   the above described alloy be $0.2 \leq Z \leq 3$, supposing that m_1 is the mass of Sn_4Ni_3 phase, m_2 is the mass of Sn phase, and $Z = m_1 / m_2$.

With this ratio being adopted, battery swelling can be reduced in the charge/discharge process at a low temperature not higher than 0 °C and, in addition, the alloy can be ground readily, so that its particle

25   size control becomes easy, and this makes it possible to reduce the negative electrode manufacturing time and the cost.

In addition, it is preferable that the above described composite layer contain carbon material, thereby allowing battery swelling to be much more reduced in the charge/discharge process at a low

30   temperature not higher than 0 °C. When carbon material is contained, supposing that n_1 is the mass of the above described alloy, n_2 is the mass of carbon material, and $S = n_1 / n_2$, it is more preferable that S fall within the range of $0.05 \leq S \leq 3.5$. This allows battery swelling in the charge process at a low temperature to be much more reduced.

35   In addition, when powdered negative active material is used in a composite layer, it is preferable that the porosity of the above

described composite layer be 30 to 75 %. The reason for this is that cycle performance and energy density can be further enhanced.

In addition, it is preferable that the apparent density of the above described negative electrode be 2.5 to 8.3 g/cm³. The reason for this is that cycle performance and energy density can be further enhanced.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a view showing the relationship between the mass fraction of tin and the energy density.

Fig. 2 is a view showing the relationship between the mass fraction of tin and the capacity retention at the 30th cycle.

Fig. 3 is a view showing the relationship between the porosity of the negative composite layer and the energy density.

Fig. 4 is a view showing the relationship between the porosity of the negative composite layer and the capacity retention.

Fig. 5 is a view showing the X-ray diffraction pattern of alloy X used in Embodiment 19.

Fig. 6 is a view showing the relationship between battery swelling and Z.

Fig. 7 is a view showing the relationship between battery swelling and S.

Fig. 8 is a view showing the X-ray diffraction pattern of alloy Y used in Embodiment 32.

PREFERRED EMBODIMENTS OF THE INVENTION

The present invention provides a non-aqueous electrolyte secondary battery comprising a negative electrode with a composite layer containing a negative active material, a positive electrode, and a non-aqueous electrolyte; characterized in that said negative active material is an alloy containing 5 to 25 mass% of nickel (Ni) and 75 to 95 mass% of tin (Sn), and that such alloy contains Sn_4Ni_3 phase and Sn phase. In the above described ranges of 5 to 25 and 75 to 95, the values were expressed by the figures which were rounded to the nearest integer.

In the above described alloy, elements other than Sn and Ni

may be contained; for example, nonmetallic elements such as N, P, C, O, etc., or metallic elements such as Cu, Co, Fe, Ag, Pb, etc. may be contained.

In addition, in the above described alloy, crystalline phases or noncrystalline phases other than Sn_4Ni_3 phase and Sn phase may be contained; for example, the phases containing Sn and Ni such as Sn_2Ni_3 phase, Sn-Ni amorphous phase, etc., the phases consisting of other elementary substances such as Cu phase, Fe phase, etc., and the phases containing other elements such as Ag_3Sn phase, Si_2Ni phase, etc. may be contained. In addition, this material may be an intermetallic compound, a solid solution or a mixture thereof, or may be eutectic or peritectic.

In the X-ray diffraction obtained with CuKα radiation, the alloy to be used in the present invention has peaks which lie in the ranges of $30.1° \leq 2\theta \leq 30.4°$ and $30.5° \leq 2\theta \leq 30.8°$. The peak lying in the range of $30.1° \leq 2\theta \leq 30.4°$ is attributed to Sn_4Ni_3 and the one in the range of $30.5° \leq 2\theta \leq 30.8°$ is attributed to Sn. Only Sn phase is capable of inserting/extracting Li reversibly, and Sn_4Ni_3 phase is not. Sn_4Ni_3 phase serves as the matrix capable of electronic conduction which supports Sn phase and, in the charge/discharge reaction of Sn phase, the matrix of Sn_4Ni_3 phase holds the crystalline structure; therefore, the charge/discharge cycle performance of Sn-Ni alloy is believed to improve. In the X-ray diffraction pattern, a peak indicates a local maximal value of diffraction intensity.

In addition, when the amounts of Ni and Sn contained in the alloy fall outside the ranges of 5 to 25 mass% and 75 to 95 mass%, respectively, a deterioration in cycle performance or a decrease in capacity is caused.

Concerning the manufacturing method for the alloy to be used in the present invention, various methods can be applied: for example, a method of cooling a molten metal on a water cooled copper hearth and the like after the molten metal was prepared by dissolving and mixing the metals such as Sn, Ni, etc. in an arc melting furnace and the like; electroplating method; electroless plating method; sputtering method; vacuum evaporation method; mechanical milling method; gas atomization method, etc.

When the molten metal cooling method described above is used, it is desirable that the cooling rate of molten metal fall within the range of 1×10^2 °C/sec to 5×10^4 °C/sec. When the cooling rate of molten metal is not less than 1×10^2 °C/sec, it is possible to obtain an alloy in which the fine crystallites of Sn phase and Sn_4Ni_3 phase are uniformly contained. Hence, it is desirable that the cooling rate of molten metal be not less than 1×10^2 °C/sec. In addition, in order to set the cooling rate of molten metal greater than 5×10^4 °C/sec, huge facilities are required; hence, it is desirable that the cooling rate of molten metal be not greater than 5×10^4 °C/sec. When Sn and Ni are melted together and then quickly cooled under the above described conditions, the uniform mixed alloy of Sn phase and Sn_4Ni_3 phase thus prepared; therefore, cycle performance becomes satisfactory.

The manufacturing method for the alloy to be used in the present invention is not considered limited to the above described manufacturing methods. Electroplating method is also a preferable one. The reason for this is that the part which is obtained by electroplating Sn-Ni alloy on a substrate can be readily used as the negative electrode of a non-aqueous electrolyte battery; hence the negative electrode manufacturing time can be reduced significantly.

As the substrate to be used for electroplating, it is preferable that a plane, three-dimensional pored structure or network structure having Cu or Ni as a major component be used. Here, having Cu or Ni as a major component means that Cu or Ni content (mass%) is the highest in the respective contents of the components which make up the substrate. Examples for those having Cu or Ni as a major component include pure Cu foil, pure Ni foil, their alloy doped with trace amounts of metals, surface-treated Cu foil, etc. Concrete examples of a plane structure are, for example, a foil, a plate, etc.; those of a three-dimensional pored structure are, for example, a foam body, a sintered body, etc.; and those of a network structure are, for example, an expanded lattice, a punching metal, a mesh, etc.

It is preferable that the ratio of Sn_4Ni_3 phase to Sn phase in the manufacturing of alloy be $0.2 \leq Z \leq 3$, supposing that m_1 is the mass of Sn_4Ni_3 phase, m_2 is the mass of Sn phase, and $Z = m_1 / m_2$. The reason for this is that battery swelling can be reduced in the charge/discharge

process at a low temperature not higher than 0 °C, and that the alloy can be ground readily.

The negative electrode to be used in the present invention has a composite layer containing the above described alloy as a negative active material, and it is preferable that the composite layer contain carbon material.

In the non-aqueous electrolyte secondary battery which was produced using the negative electrode where the negative active material contained in the composite layer consists of the above described alloy alone, the above described alloy expands significantly during charge; hence, when charged fast at a temperature of 0 °C, the battery swells significantly. In addition, in the non-aqueous electrolyte secondary battery which was produced using the negative electrode where the negative active material contained in the composite layer consists of carbon material alone, the amount of metallic lithium deposition on the surface of the carbon material during charge is large; hence, when charged fast at a temperature of 0 °C, the battery swells significantly.

Meanwhile, in the non-aqueous electrolyte secondary battery which was produced using the negative electrode where the negative active material contained in the composite layer consists of the above described alloy and carbon material, battery swelling is reduced. The reason for this is believed to be that the above described alloy reduces the lithium deposition on the surface of the carbon material, and that the carbon material reduces the nonuniformity of current distribution, which occurs from a decrease in current collection at the composite layer caused due to alloy expansion, and the resultant lithium deposition, that is, reduces the deterioration of current collection.

When carbon material is contained in the composite layer, supposing that n_1 is the mass of the above described alloy, n_2 is the mass of carbon material, and S (= n_1/n_2) is the ratio of n_1 to n_2, it is preferable that S fall within the range of $0.05 \leq S \leq 3.5$.

When S value is either smaller than 0.05 or greater than 3.5, battery swelling cannot be reduced sufficiently. This is believed to be due to the insufficiency of the above described mechanism.

Concerning the above described carbon material, the material is

not to be considered limited specifically; for example, it is possible to use graphitic carbon materials such as natural graphite, artificial graphite, etc., acetylene black, ketjen black, vapor grown carbon fiber, cokes, pyrolytic carbon, activated carbon, or mixtures thereof. The form
5   is not limited specifically; for example, scale-like, fiber-like, spherical, or massive form is included. In addition, boron, aluminum, etc. may be added to the carbon material.

       When a powdered negative active material is used for a composite layer, it is preferable that the porosity of the above described
10   composite layer fall within the range of 30 to 75 %. With this range being adopted, cycle performance can be further enhanced and battery energy density can be much increased. When the porosity is less than 30 %, cycle performance deteriorates, and when it is greater than 75 %, battery energy density decreases.

15   When a negative electrode is prepared according to the following manner; for example, a paste is prepared by mixing a negative active material, a binder and a disperse medium, followed by this paste is coated on a metal foil, and later on only the disperse medium is removed; a composite layer refers to the portion combining
20   the active material and the binder except a metal foil portion in the negative electrode. In addition, when a negative electrode is prepared by synthesizing Sn·Ni alloy on a foil substrate using electroplating method, it refers to the Sn·Ni alloy portion except the foil substrate portion in the negative electrode. In this case, a binder is not contained
25   in the composite layer.

       The porosity of a composite layer shall be defined by the following equations:

       [Porosity of a composite layer] (%) = 100 − [true volume of the composite] / [apparent volume of the composite layer] × 100,
30   [True volume of the composite] = [mass of the composite layer] / [average density of the material composing the composite layer].

       In addition, it is preferable that the apparent density of a negative electrode fall within the range of 2.5 to 8.3 g/cm^3. With this range being adopted, cycle performance can be further improved and
35   battery energy density can be much increased.

       When the apparent density of a negative electrode is less than

2.5 g/cm³, the volume occupied by a current collector is small; therefore, an increase in internal resistance or the cutting of an electrode plate tends to occur, and cycle performance deteriorates significantly. In addition, when the apparent density of a negative electrode is greater

5   than 8.3 g/cm³, the proportion occupied by a current-collector in the negative electrode declines and the amount of active material per unit volume in the negative electrode decreases; therefore, the energy density becomes less than those of graphite/lithium transition metal oxides which have been well known.

10   The apparent density of a negative electrode is defined by the following equation:

[Apparent density of a negative electrode] = [mass of the negative electrode] / [apparent volume of the negative electrode].

In the non-aqueous electrolyte secondary battery of the present

15   invention, any shapes may be applied to the positive electrode and the negative electrode; for example, sheet type, pellet type, etc. can be used. As concrete examples of a sheet-type electrode plate, the one prepared by placing on a metal foil a composite layer containing an active material, the one prepared by filling a metal foam with a composite

20   containing an active material, etc. are included. As concrete examples of a pellet-type electrode plate, the one obtained by press molding a composite containing an active material, the one prepared by filling a metal can with a composite containing an active material, etc. are included.

25   In addition, it is preferable that the positive and negative electrodes contain current collector substrates; for example, a plane structure such as copper, nickel, aluminum, etc., a three-dimensional porosity structure, or a network structure be applicable. Concrete examples of the plane structure are, for example, a foil, a plate, etc.;

30   those of the three-dimensional porosity structure are, for example, a foam body, a sintered body, etc.; and those of the network structure are, for example, an expanded lattice, a punching metal, a mesh, etc.

As the non-aqueous electrolyte to be used in the non-aqueous electrolyte secondary battery of the present invention, a non-aqueous

35   electrolyte solution or a solid electrolyte can be used without specific limitation.

For example, when a non-aqueous electrolyte solution is used, the following polar solvents or the mixed solvents arbitrarily containing them can be used as the solvent: ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, methyl

5   ethyl carbonate, γ-butyrolactone, sulfolane, dimethyl sulfoxide, acetonitrile, dimethyl formamide, dimethyl acetamide, 1,2-dimethoxyethane, 1,2-diethoxyethane, tetrahydrofuran, 2-methyl tetrahydrofuran, dioxolane, methyl acetate, ethyl acetate, etc.

In addition, as the solute, the following lithium salts or

10   mixtures thereof can be used: $LiPF_6$, $LiBF_4$, $LiAsF_6$, $LiClO_4$, $LiSCN$, LiI, $LiCl$, $LiBr$, $LiCF_3CO_2$, $LiCF_3SO_3$, $LiC_4F_9SO_3$, $LiN(SO_2CF_3)_2$, $LiN(SO_2 CF_2CF_3)_2$, $LiN(SO_2CF_3)$ $(SO_2CF_2CF_2CF_2CF_3)$, $LiN(COCF_3)_2$, $LiN(COC F_2CF_3)_2$, etc.

When a solid electrolyte is used, it is possible to use, for

15   example, an inorganic solid electrolyte such as Li-containing chalcogenide, etc., a single ion conductor consisting of Li^+-containing polymer, a polymer electrolyte where lithium salt is contained in a polymer, etc. Concerning the polymer electrolyte, lithium salt may be contained in a polymer by wetting or swelling the polymer with a

20   non-aqueous electrolyte solution, or lithium salt alone may be dissolved in a polymer.

As the lithium salt to be contained in the polymer electrolyte, the following lithium salts or mixtures thereof can be used: $LiPF_6$, $LiBF_4$, $LiAsF_6$, $LiClO_4$, $LiSCN$, LiI, $LiCl$, $LiBr$, $LiCF_3CO_2$, $LiCF_3SO_3$,

25    $LiC_4F_9SO_3$, $LiN(SO_2CF_3)_2$, $LiN(SO_2 CF_2CF_3)_2$, $LiN(SO_2CF_3)$ $(SO_2CF_2CF_2CF_2CF_3)$, $LiN(COCF_3)_2$, $LiN(COC F_2CF_3)_2$, etc. Moreover, when a solid electrolyte is used, several electrolytes may be contained in a battery. For example, different electrolytes can be used in the positive electrode and the negative electrode, respectively.

30   As the polymer to be used for the polymer electrolyte, it is preferable that it exhibit satisfactory ion conductivity when wetted or swelled with a non-aqueous electrolyte solution; for example, polyether such as poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), etc., poly(vinylidene fluoride) (PVdF), poly(vinyl chloride) (PVC),

35   polyacrylonitrile (PAN), poly(vinylidene chloride), poly(methyl methacrylate), poly(methyl acrylate), poly(vinyl alcohol),

polyacrylonitrile, polymethacrylonitrile, poly(vinyl acetate), polyvinylpyrrolidone, polyethyleneimine, polybutadiene, polystyrene, polyisoprene, or derivatives thereof can be used alone or by mixture. In addition, it is also possible to use polymers prepared by

5 copolymerization of each monomer composing the above described polymers; for example, vinylidene fluoride/hexafluoropropylene copolymer (P(VdF/HEP)), styrene-butadiene rubber (SBR), etc.

The reason for using these polymer electrolytes is that the Li^+ ion conductivity and mobility are enhanced, so that battery polarization

10 can be minimized. In addition, it is preferable that a polymer electrolyte be free to change in shape. The reason for this is that it is possible to follow the volume expansion/contraction of a negative active material due to charge/discharge, thereby allowing the electronic conduction performance and ion conduction performance of the negative

15 electrode to be maintained satisfactory.

In the non-aqueous electrolyte secondary battery of the present invention, the negative electrode or positive electrode (or both of them) may contain a polymer electrolyte. It is preferable that this polymer electrode exhibit lithium ion conductivity and binding property. The

20 reason for this is that the binding property between active material and active material and between active material and polymer electrolyte is satisfactory in this negative electrode or positive electrode, and that the electronic conduction performance and ion conduction performance of the negative electrode can be maintained satisfactory. Especially, it

25 is preferable that the polymer electrolyte be porous. The reason for this is that holding electrolyte solution in a pore causes the ion conductivity of polymer electrolyte to further improve.

As the positive active material to be used in the non-aqueous electrolyte secondary battery of the present invention, the following can

30 be used: for example, composite oxides expressed by composition formulas Li_xMO_2, $Li_xM_yM'_zO_2$ or $Li_yM_2O_4$ (where M and M' are transition metals, $0 \leq x \leq 1$, $0 \leq y \leq 2$, and y+z=1 or 2), oxides having tunnel-like holes, metal chalcogenide having layer structures, etc. As concrete examples of them, $LiCoO_2$, $LiNiO_2$, $LiCo_{0.2}Ni_{0.8}O_2$,

35 $LiCo_{0.15}Ni_{0.85}O_2$, $LiNi_{0.5}Mn_{1.5}O_2$, $LiMn_2O_4$, $LiMnO_2$, MnO_2, FeO_2, V_2O_5, V_6O_{13}, TiO_2, TiS_2, $NiOOH$, $FeOOH$, FeS, etc. are included. Each active

material described above may be used in arbitrary mixture.

When a material not containing Li, such as MnO_2, FeO_2, V_2O_5, V_6O_{13}, TiO_2, TiS_2, $NiOOH$, $FeOOH$, FeS, etc., is used as the positive active material, a battery may be produced using the one in which Li^+ is chemically inserted in the positive electrode or negative electrode. For example, a case of using the one prepared by bringing the positive electrode or negative electrode into contact with metallic lithium in a non-aqueous electrolyte containing Li^+, a case of attaching metallic Li on the surface of the positive electrode or negative electrode, etc. are included.

In addition, a separator may be used in the non-aqueous electrolyte secondary battery of the present invention. For example, an insulating polyolefin microporous membrane, an inorganic solid electrolyte membrane, a polymer electrolyte membrane, etc. can be applied. In addition, it is also possible to use an insulating microporous membrane in combination with a polymer electrolyte.

In addition, a form of battery case can be selected from, for example, a prismatic shape, a cylindrical shape, an elliptic cylindrical shape, the one fabricated with sheet material in an envelop-like shape, the one processed by molding the sheet which was prepared by coating metallic, such as aluminum, sheet with resin, etc. As the material of battery case, it is possible to select a material mainly composed of, for example, iron, aluminum, etc.

Embodiments

Hereinafter, preferred embodiments of the present invention will be described; however, the scope of application of the present invention will not be limited to them.

Embodiment 1

In this example, Sn powder and Ni powder were weighed out to 95 mass% and 5 mass%, respectively, and preparatively mixed in a mortar. This mixed powder and SUS balls for ball-milling were enclosed in a SUS hermetically-sealed container for the ball-milling under an argon atmosphere. Subsequently, this container was set in a planetary ball mill, the powder inside was milled for 30 minutes, and the obtained powder was dried at 150 °C, thereby producing an alloy containing 95

mass% of Sn and 5 mass% of Ni. This alloy was used as the negative active material.

A paste was mixed and prepared so as to consist of 45 mass% of the powdered negative active material above described, 10 mass% of
5　PVdF as a binder and 45 mass% of N-methyl-2-pyrrolidone (NMP), and applied to both surfaces of Cu foil of 27 mm in width and 10 μm in thickness; the coated foil was dried at 150 °C to evaporate NMP and then pressed to adjust the porosity; and thus the negative electrode was produced.

10　A paste was mixed and prepared so as to consist of 70 mass% of lithium cobalt oxide, 6 mass% of acetylene black, 9 mass% of PVdF and 15 mass% of NMP, and applied to both surfaces of aluminum foil of 27 mm in width and 15 μm in thickness; the coated foil was dried at 150 °C to evaporate NMP and then pressed; and thus the positive electrode
15　was produced.

These positive and negative electrodes and a polyethylene separator of 29 mm in width and 25 μm in thickness were wound and then inserted into a stainless case of 47.5 mm in height, 29.2 mm in width and 4.55 mm in thickness. Furthermore, positive and negative
20　leads were welded on to the positive and negative terminals located on the cover of the battery case, respectively, by means of ultrasonic welding, and then the cover was joined to the battery case by laser welding.

A mixed solution containing 1 mol/l of LiPF$_6$ dissolved in a
25　mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) in a volume ratio of 1 : 1 was used as an electrolyte. This electrolyte solution was poured through a filling opening of 1 mm in diameter provided on the battery case, and then the opening was sealed by laser welding. Battery assembly was implemented inside a dry room at 25 °C.
30　According to the above described procedures, Battery (A) of Embodiment 1 was manufactured.

Embodiments 2 to 4

To these examples, alloy compositions shown in Table 1 were applied, where the weighing amounts of Sn powder and Ni powder were
35　varied in the course of the preparation of the negative active material; except for the above, Batteries (B) to (D) of Embodiments 2 to 4 were

manufactured in an identical manner to that of Embodiment 1.

Comparative Examples 1 to 3

To these examples, alloy compositions shown in Table 1 were applied, where the weighing amounts of Sn powder and Ni powder were
5   varied in the course of the preparation of the negative active material; except for the above, Batteries (E) to (G) of Comparative Examples 1 to 3 were manufactured in an identical manner to that of Embodiment 1.

Comparative Example 4

In this example, Sn powder and Ni powder were weighed out to
10   77 mass% and 23 mass%, respectively, mixed in a mortar, and used as the negative active material without mechanical milling; except for the above, Battery (H) of Comparative Example 4 was manufactured in an identical manner to that of Embodiment 1.

Table 1 shows details of Batteries (A) to (D) of Embodiments 1
15   to 4 and Batteries (E) to (H) of Comparative Examples 1 to 4.

(Table 1)

	Battery	Alloy composition used for negative active material mass%		Porosity of negative composite layer %	Appearance of XRD peak	
		Sn	Ni		$30.1° \leq 2\theta \leq 30.4°$	$30.5° \leq 2\theta \leq 30.8°$
Comparative Example 1	E	100	0	50	Appeared	Appeared
Comparative Example 2	F	97	3	50	Appeared	Appeared
Embodiment 1	A	95	5	50	Appeared	Appeared
Embodiment 2	B	93	7	50	Appeared	Appeared
Embodiment 3	C	77	23	50	Appeared	Appeared
Embodiment 4	D	75	25	50	Appeared	Appeared
Comparative Example 3	G	73	27	50	Appeared	Appeared
Comparative Example 4	H	77	23	50	Not appeared	Appeared

Battery Evaluation Test

Using Batteries (A) to (H), a charge/discharge test was conducted in an incubator kept at 25 °C. In this test, each battery was
20   charged at a constant current of 40 mA until the voltage reached 4.1 V and subsequently charged for 2 hours at a constant voltage of 4.1 V, and

then discharged at a constant current of 160 mA until the voltage dropped to 2.7 V: taking these steps as one cycle, charge/discharge was repeated 30 cycles. The discharge capacity, volumetric energy density and coulombic efficiency at the 1st cycle of each battery, and the

5   capacity retention at the 30th cycle were determined. Here, the coulombic efficiency at the 1st cycle (%) and the capacity retention at the 30th cycle (%) shall be defined by the following equations:

[Coulombic efficiency at the 1st cycle] = [discharge capacity at the 1st cycle] / [quantity of electric charge at the 1st cycle] × 100

10   [Capacity retention at the 30th cycle] = [discharge capacity at the 30th cycle] / [discharge capacity at the 1st cycle] × 100

Comparative Example 5

In this example, a paste was mixed and prepared so as to consist of 50 mass% of powdered graphitic carbon, 5 mass% of PVdF

15   and 45 mass% of NMP, and applied to both surfaces of Cu foil of 27 mm in width and 14 μm in thickness; the coated foil was dried at 150 °C to evaporate NMP and then pressed; and thus the negative electrode was produced. Except for using this negative electrode, Battery (I) of Comparative Example 5 was manufactured in an identical manner to

20   that of Embodiment 1.

Using Battery (I), a charge/discharge test was conducted in an incubator kept at 25 °C. In this test, each battery was charged at a constant current of 40 mA until the voltage reached 4.1 V and subsequently charged for 2 hours at a constant voltage of 4.1 V, and

25   then discharged at a constant current of 160 mA until the voltage dropped to 2.7 V: taking these steps as one cycle, charge/discharge was repeated 30 cycles.

The discharge capacity, volumetric energy density and coulombic efficiency at the 1st cycle and the capacity retention at the

30   30th cycle of each battery were determined.

Table 2 shows the measurement results for Batteries (A) to (I). In addition, the relationship between the mass fraction of the tin contained in the alloy used as the negative active material and the energy density was illustrated in Fig. 1, and the relationship between

35   the mass fraction of the tin contained in the alloy used as the negative active material and the capacity retention at the 30th cycle was

illustrated in Fig. 2.

(Table 2)

	Battery	1st cycle			30th cycle
		Discharge capacity mAh	Energy density Wh/L	Coulombic efficiency %	Capacity retention %
Comparative Example 1	E	1000	512	85	40
Comparative Example 2	F	963	494	88	75
Embodiment 1	A	956	490	88	95
Embodiment 2	B	940	480	88	96
Embodiment 3	C	830	425	90	99
Embodiment 4	D	786	403	90	99
Comparative Example 3	G	704	360	90	99
Comparative Example 4	H	830	425	65	20
Comparative Example 5	I	610	390	90	99

In Battery (I) of Comparative Example 5, where conventional graphitic carbon powder was used as the negative active material, the

5   energy density is 390 Wh/L. Accordingly, in order to have a battery whose energy density is higher than that of the conventional type, the energy density of the battery is required to exceed 390 Wh/L. In addition, the coulombic efficiency should be not less than 84 %. The reason for this is that when coulombic efficiency is less than 84 %,

10   metallic Li deposition on the surface of the negative electrode tends to occur easily during charge, and accordingly that a decrease in safety or an increase in battery swelling is caused. The capacity retention at the 30th cycle has to be not less than 60 %, and preferably not less than 85 %. This is due to the reason that the capacity retention at the 30th

15   cycle being less than 60 % is not suitable for practical use for a secondary battery, and that that of less than 85 % is not appropriate when prolonged use is expected.

From Fig. 1, it is found that when the tin contained in the alloy is less than 75 mass%, the energy density drastically decreases down to

20   390 Wh/L or less. In addition, from Fig. 2, it is found that when the tin contained in the alloy exceeds 95 mass%, the capacity retention at the

30th cycle drastically decreases to less than 60 %. Accordingly, the alloy should contain 75 to 95 mass% of tin.

Likewise, it is found that when the nickel contained in the alloy is greater than 25 mass%, the energy density drastically decreases to 390 Wh/L or less. In addition, it is found that when the nickel contained in the alloy is less than 5 mass%, the capacity retention at the 30th cycle drastically decreases to less than 60 %. Accordingly, the alloy should contain 5 to 25 mass% of nickel.

In addition, peaks in an X-ray diffraction pattern were noted to lie in both ranges of $30.1° \leq 2\theta \leq 30.4°$ and $30.5° \leq 2\theta \leq 30.8°$; in Batteries (A) to (D) of Embodiments 1 to 4, where the alloy containing Sn_4Ni_3 phase and Sn phase is used as the negative active material, the capacity retention at the 30th cycle was found to be as high as 95 % or more. On the other hand, in Battery (H), where the peak lay only in the latter range, the capacity retention at the 30th cycle was found to be as remarkably low as 20%. XRD analysis was conducted by means of a powder diffraction method with CuKα radiation, and the finding that the above described two layers were contained in the alloy was confirmed by using EPMA, as well as the peak analysis by XRD. Hereinafter, for the materials prepared by means of ball milling, confirmation was performed in the same manner.

Embodiment 5

In this example, Cu foil of 27 mm in width and 14 μm in thickness was immersed in a commercially manufactured Sn-Ni plating solution (Kojundo Chemical Lab. Co., Ltd., SNS-200E). After that, using the Sn-Ni alloy containing 28 mass% of Ni in the counter electrode, electricity was conducted so that the cathode current density becomes 2 A/dm^3, and Sn-Ni alloy was synthesized on the Cu foil. After washed with ion exchange water, this material was dried at 150 °C, and thus the negative electrode was prepared. As a result of conducting the quantitative analysis of element, the composition of this Sn-Ni alloy was found to be 85 mass% of Sn and 15 mass% of Ni. In addition, in the X-ray diffraction pattern of this Sn-Ni alloy, the peaks due to CuKα radiation lay at $2\theta = 30.3°$ and $30.6°$. Except for using this negative electrode, Battery (J) of Embodiment 5 was manufactured in an identical manner to that of Embodiment 1.

Embodiments 6 to 12

In these examples, Sn powder and Ni powder were weighed out to 85 mass% and 15 mass%, respectively, to make the alloy containing 85 mass% of tin and 15 mass% of nickel, the obtained material was used as the negative active-material, and the porosities of the negative composite layer were varied, as shown in Table 3, by pressing; except for the above, Batteries (K) to (Q) of Embodiments 6 to 12 were manufactured in an identical manner to that of Embodiment 1.

Table 3 shows details of Batteries (J) to (Q).

(Table 3)

	Battery	Porosity of negative composite layer %	Appearance of XRD peak	
			$30.1°\leq 2\theta \leq 30.4°$	$30.5°\leq 2\theta \leq 30.8°$
Embodiment 5	J	· ·	Appeared	Appeared
Embodiment 6	K	28	Appeared	Appeared
Embodiment 7	L	30	Appeared	Appeared
Embodiment 8	M	32	Appeared	Appeared
Embodiment 9	N	50	Appeared	Appeared
Embodiment 10	O	73	Appeared	Appeared
Embodiment 11	P	75	Appeared	Appeared
Embodiment 12	Q	77	Appeared	Appeared

Concerning Batteries (J) to (Q) of Embodiments 5 to 12, the discharge capacity, volumetric energy density and coulombic efficiency at the 1st cycle, and the capacity retention at the 30th cycle were obtained under the same conditions as Battery (A) of Embodiment 1. The results are shown in Table 4.

(Table 4)

	Battery	1st cycle			30th cycle
		Discharge capacity mAh	Energy density Wh/L	Coulombic efficiency %	Capacity retention %
Embodiment 5	J	906	465	92	100
Embodiment 6	K	890	457	84	60
Embodiment 7	L	877	450	86	90
Embodiment 8	M	863	443	86	95
Embodiment 9	N	854	428	89	97
Embodiment 10	O	848	415	91	98
Embodiment 11	P	840	409	91	98
Embodiment 12	Q	803	391	91	98

In a comparison between the battery of Embodiment 5, where the alloy made by electroplating was applied to the negative active material, and Batteries (K) to (Q) of Embodiments 6 to 12, where the

5 alloy made by mechanical milling was applied to the negative active material, the former showed higher values than the latter in every item in the discharge capacity, volumetric energy density and coulombic efficiency at the 1st cycle, and the capacity retention at the 30th cycle. Based on this finding, it is obvious that electroplating is preferable as

10 an alloy manufacturing process.

Table 3 shows the relationship between the porosity of the negative composite layer and the energy density. In addition, Table 4 shows the relationship between the porosity of the negative active material layer and the capacity retention.

15 From Fig. 3, it is found that when the porosity of the negative composite layer exceeds 75 %, the energy density drastically decreases. In addition, from Fig. 4, when the porosity of the negative composite layer is less than 30 %, the capacity retention remarkably decreases. Accordingly, when powdered negative active material is used for the

20 composite layer, it is preferable that the porosity of the negative composite layer fall within the range of 30 % to 75 %.

Embodiments 13 to 15

In these examples, the thicknesses of the Cu foil serving as the substrate in electroplating were varied as shown in Table 5; except for the above, Batteries (R) to (T) of Embodiments 13 to 15 were manufactured in an identical manner to that of Embodiment 5.

5 **Embodiments 16 to 18**

In these examples, the thicknesses of the Cu foil to be used for the negative current collector were varied as shown in Table 5; except for the above, Batteries (U) to (W) of Embodiments 16 to 18 were manufactured in an identical manner to that of Embodiment 6.

10 Table 5 shows details of Batteries (R) to (W) of Embodiments 13 to 18.

(Table 5)

	Battery	Thick-ness of Cu foil μm	Apparent density of negative electrode g/cm^3	Porosity of negative composite layer %	Appearance of XRD peak	
					30.1° $\leqq 2\theta \leqq$ 30.4°	30.5° $\leqq 2\theta \leqq$ 30.8°
Embodiment 13	R	4	2.2	--	Appeared	Appeared
Embodiment 14	S	8	2.5	--	Appeared	Appeared
Embodiment 15	T	12	2.8	--	Appeared	Appeared
Embodiment 16	U	45	8.2	30	Appeared	Appeared
Embodiment 17	V	50	8.3	30	Appeared	Appeared
Embodiment 18	W	55	8.4	30	Appeared	Appeared

Concerning Batteries (R) to (W) of Embodiments 13 to 18, the discharge capacity, volumetric energy density and coulombic efficiency

15 at the 1st cycle, and the capacity retention at the 30th cycle were determined under the same conditions as Battery (A) of Embodiment 1. The results are shown in Table 6.

(Table 6)

| | Battery | 1st cycle | | | 30th cycle |
		Discharge capacity mAh	Energy density Wh/L	Cloulombic efficiency %	Capacity retention %
Embodiment 13	R	890	457	86	60
Embodiment 14	S	877	450	86	90
Embodiment 15	T	863	443	86	95
Embodiment 16	U	848	415	91	98
Embodiment 17	V	840	409	91	98
Embodiment 18	W	803	391	91	98

In Batteries (R) to (T) of Embodiments 13 to 15, when the apparent density of the negative electrode is less than 2.5 g/cm³, the capacity retention remarkably decreases. Accordingly, it is preferable that the apparent density of the negative electrode be not less than 2.5 g/cm³.

In addition, in Batteries (U) to (W) of Embodiments 16 to 18, when the apparent density of the negative electrode exceeds 8.3 g/cm³, the energy density remarkably decreases. Accordingly, it is preferable that the apparent density of the negative electrode be not greater than 8.3 g/cm³.

Based on the findings above described, it was revealed that the preferable apparent density of the negative electrode lay in the range of 2.5 g/cm³ to 8.3 g/cm³.

Embodiment 19

In this example, required amounts of Sn powder and Ni powder were respectively weighed out and preparatively mixed in a mortar. This mixed powder was press molded into pellet form, and then placed on a water cooled copper hearth in an arc melting furnace. After the furnace atmosphere was substituted with Ar atmosphere, the pellet was melted by the irradiation of arc discharge, which was stopped after the molten metal was observed to have been mixed sufficiently. The molten metal was cooled by the water cooled copper hearth and formed a button-like solid. The cooling rate of the molten metal on the water cooled copper hearth was 3×10^2 °C /sec.

The obtained button-like solid was polished until the surface had a metallic luster, the polished one was then ground, and thus alloy X was obtained. From the X-ray diffraction pattern (X-ray source: CuKa, and measurement range: 28° ≤ 2θ ≤ 42°) shown in Fig. 5, it was noted

5 that this material contained only Sn phase and Sn_4Ni_3 phase.

The quantitative analysis of element was conducted for this alloy X using ICP emission spectrometry. Supposing that the masses of the starting materials, Sn and Ni elements, are respectively p mass% and q mass%, and those of Sn phase and Sn_4Ni_3 phase in alloy X are

10 respectively v mass% and w mass%. This alloy X consists of only Sn phase and Sn_4Ni_3 phase; hence the following relational expressions are formulated between them.

p = [mass of Sn phase] + [mass of Sn in Sn_4Ni_3 phase]

= v + w × [formula mass of Sn] / [formula mass of Sn_4Ni_3]

15 = v + w × 474.8 / 650.9

q = w × [mass of Ni in Sn_4Ni_3 phase]

= w × [formula mass of Ni] / [formula mass of Sn_4Ni_3]

= w × 176.1 / 650.9

Using the p and q values obtained by the quantitative analysis

20 of element, the above described relational expressions were solved simultaneously to determine the values of v and w. Furthermore, using these values, Z (= v/w) was accordingly found to be 0.2.

A mixture was prepared so as to consist of 20 mass% of the above described alloy X and 80 mass% of graphite, mixed sufficiently in

25 a mortar, and then used as the negative active material. In this negative active material, it was found that S = 0.25. A paste was mixed and prepared so as to consist of 50 mass% of this negative active material, 5 mass% of PVdF and 45 mass% of NMP, and applied to both surfaces of Cu foil of 27 mm in width and 10 μm in thickness; the coated

30 foil was dried at 150 °C to evaporate NMP and then pressed to adjust the porosity; and thus the negative electrode having the negative composite layer on the copper foil was provided.

In this negative electrode, the mass of the negative composite layer per unit area of one side surface of the current collector was set to

35 be 7.23 mg/cm² so that the designed capacity of a completed battery can be 695 ± 5 mAh. Here, the designed capacity refers to the discharge

capacity which can be obtained in the following steps: in an incubator kept at 25 °C, a battery was charged at a constant current of 35 mA until the voltage reached 4.1 V and subsequently charged for 2 hours at a constant voltage of 4.1 V, and then discharged at a current of 140 mA

5   until the voltage dropped to 2.7 V. (Hereinafter, referred to simply as designed capacity.)

A paste was mixed and prepared so as to consist of 78 mass% of lithium cobalt oxide, 3 mass% of acetylene black, 4 mass% of PVdF and 15 mass% of NMP, and applied to both surfaces of aluminum foil of 26

10   mm in width and 15 μm in thickness; the coated foil was dried at 150 °C to evaporate NMP and then pressed; and thus the positive electrode having the positive composite layer on the aluminum foil was provided.

In this positive electrode, the mass of the positive composite layer per unit area of one side surface of the current collector was set to

15   be 21.79 mg/cm^2 so that the designed capacity of a completed battery can be 695 ± 5 mAh.

These positive and negative electrodes and a polyethylene separator of 29 mm in width and 20 μm in thickness were wound and then inserted into a prismatic, aluminum battery case of 47.0 mm in

20   height, 29.2 mm in width and 4.15 mm in thickness. The total area of the portions of the positive composite layer and negative composite layer which were placed face to face were adjusted to be 2.40 × 10^2 cm^2, Furthermore, positive and negative leads were welded on to the positive and negative terminals located on the cover of the battery case,

25   respectively, by means of ultrasonic welding, and then the cover was joined to the battery case by laser welding.

A mixed solution containing 1 mol/l of LiPF$_6$ dissolved in a mixture of EC and DEC in a volume ratio of 1 : 1, and used as an electrolyte. This electrolyte solution was poured through a filling

30   opening of 1 mm in diameter provided on the battery case, and the opening was then sealed by laser welding. When calculated based on the outer size, the volume of the battery was determined to be 5.72 cm^3. Battery assembly was implemented inside a dry room at 25 °C. According to the above described procedures, two pieces of Battery (Y1)

35   of Embodiment 19 were manufactured.

Embodiments 20 to 25, Comparative Example 6 and

Embodiment 7c

By changing the weighing amounts of the starting materials, Sn powder and Ni powder, Z values of alloy X were set to lie in the range of 0.3 to 3, and the masses of the positive and negative composite layers

5   per-unit-area-of-one-side surface of the current collector were varied; except for the above, two pieces each of Batteries (Y2) to (Y7) of Embodiments 20 to 25 were manufactured in an identical manner to that of Embodiment 19.

In addition, Z value of alloy X was set to be 0.1, and the masses

10   of the positive and negative composite layers per unit area of one side surface of the current collector were changed; except for the above, two pieces of Battery (Y8) of Comparative Example 6 were manufactured in an identical manner to that of Embodiment 19; and, Z value of alloy X was set to be 4.5, and the masses of the positive and negative composite

15   layers per unit area of one side surface of the current collector were changed; except for the above, two pieces of Battery (Y9) of Embodiment 7c were manufactured in an identical manner to that of Embodiment 19.

The details of the batteries manufactured above, Embodiments

20   19 to 25, Comparative Example 6 and Embodiment 7c, were summarized in Table 7. Here, the values of the contents are expressed by the figures which were rounded to the nearest integer, the alloy contains only Sn and Ni, and confirmation that only Sn phase and Sn_4Ni_3 phase are contained has been made.

25

(Table 7)

	Battery code	Element content in alloy mass%		Porosity %	Z value of alloy X	Mass per one side surface of composite layer mg/cm²	
		Sn	Ni			Negative electrode	Positive electrode
Comparative Example 6	Y8	98	2	33	0.1	6.98	22.01
Embodiment 19	Y1	95	5	33	0.2	7.23	21.79
Embodiment 20	Y2	94	6	33	0.3	7.43	21.69
Embodiment 21	Y3	91	9	33	0.5	7.79	21.55
Embodiment 22	Y4	85	15	33	1.2	9.72	21.63
Embodiment 23	Y5	84	16	33	1.5	10.39	21.56
Embodiment 24	Y6	82	18	33	2.0	10.56	21.41
Embodiment 25	Y7	80	20	33	3.0	10.69	21.32
Embodiment 7c	Y9	78	22	33	4.5	10.84	21.24

Battery Evaluation Test

Using one piece each of Batteries (Y1) to (Y9), the thicknesses, t_1 (mm), of the batteries before charge were measured, and then they

5　were left for 3 hours in an incubator kept at 0 °C. These batteries were charged at a constant current of 1400 mA equivalent to 2C rate until the voltage reached 4.1 V and subsequently charged for 2 hours at a constant voltage of 4.1 V. Thirty minutes after completion of this charge, the thicknesses, t_2 (mm), of the batteries after charge were measured.

10　Based on the results of the above measurements, battery swelling in the fast charge process at a low temperature was determined using the following equation. The results were shown in Table 8.

[Battery swelling] (mm) = t_2 (mm) − t_1 (mm)

It is not appropriate to use the battery which swells more than

15　0.25 mm for the purpose of power supply for portable electronics such as cellular phones because of a risk of battery pack failure. Accordingly, battery swelling has to be not greater than 0.25 mm. Repeated charge/discharge cycles are expected to cause a battery to slightly swell; therefore, it is desirable that battery swelling be not greater than

20　0.20 mm.

Using the other piece each of Batteries (Y1) to (Y9) that were not used for the above described test, a charge/discharge test was conducted in an incubator kept at 25 °C. Each battery was charged at a constant current of 35 mA until the voltage reached 4.1 V and

5   subsequently charged for 2 hours at a constant-voltage-of 4.1 V, and then discharged at a current of 140 mA until the voltage dropped to 2.7 V: taking these steps as one cycle, charge/discharge was repeated 50 cycles. Using the discharge capacity at the 1st cycle and that at the 50th cycle, capacity density and the capacity retention at the 50th cycle

10   were calculated according to the following equations;

[Capacity density, mAh/cm^3] = [discharge capacity at the 1st cycle, mAh] / [battery volume, cm^3]

[Capacity retention at the 50th cycle, %] = [discharge capacity of the 50th cycle, mAh] / [discharge capacity at the 1st cycle, mAh]

15   The test results were summarized in Table 8.

(Table 8)

	Battery code	Battery swelling mm	Discharge capacity at the 1st cycle mAh	Capacity density mAh/cm^3	Capacity retention at the 50th cycle %
Comparative Example 6	Y8	0.21	693	121	91.5
Embodiment 19	Y1	0.15	695	122	93.5
Embodiment 20	Y2	0.13	694	121	94.1
Embodiment 21	Y3	0.10	695	122	95.5
Embodiment 22	Y4	0.11	696	122	95.4
Embodiment 23	Y5	0.12	695	122	94.8
Embodiment 24	Y6	0.14	696	122	93.8
Embodiment 25	Y7	0.17	694	121	92.8
Embodiment 7c	Y9	0.23	698	122	91.5

In addition, Fig. 6 shows the relationship between the Z value, which is the ratio of the mass of Sn$_4$Ni$_3$ phase (m1) to the mass of Sn phase (m2) in alloy X used in the negative electrode of these batteries,

20   and the battery swelling. Table 8 and Fig. 6 revealed the following.

Battery swelling in the fast charge process at a low temperature in each case of Batteries (Y1) to (Y7) of Embodiments 19 to 25 was not

greater than 0.20 mm and less than those of Battery (Y8) of Comparative Example 6 and Battery (Y9) of Embodiment 7c.

In addition, capacity retention at the 50th cycle in each case of Batteries (Y1) to (Y7) of Embodiments 19 to 25 was not less than 92.5 % and greater than those of Battery (Y8) of Comparative Example 6 and Battery (Y9) of Embodiment 7c.

Moreover, discharge capacity at the 1st cycle and capacity density were almost same in Batteries (Y1) to (Y9) of Embodiments 19 to 25, Comparative Example 6 and Embodiment 7c.

Embodiment 26, Comparative Examples 8 to 10

Z value of alloy X was set to be 1.1; except for the above, two pieces of Battery (Y10) of Embodiment 26 were manufactured in an identical manner to that of Embodiment 19. In this negative electrode, the mass of the negative composite layer per unit area of one side surface of the current collector was set to be 8.35 mg/cm² and, in the positive electrode, the mass of the positive composite layer per unit area of one side surface of the current collector was set to be 21.62 mg/cm² so that the designed capacity of the completed battery can be 695 ± 5 mAh.

In the battery of Comparative Example 8, only graphite was used as the negative active material. A paste was mixed and prepared so as to consist of 50 mass% of graphite, 5 mass% of PVdF and 45 mass% of NMP; and applied to both surfaces of Cu foil of 27 mm in width and 10 μm in thickness; the coated foil was dried at 150 °C to evaporate NMP and then pressed to adjust the porosity; and thus the negative electrode was provided. Except for using this negative electrode, two pieces of Battery (Y11) of Comparative Example 8 were manufactured in an identical manner to that of Embodiment 19.

In the battery of Comparative Example 9, a mixture of a material consisting of Sn₄Ni₃ phase alone and graphite was used as the negative active material. 20 mass% of a material consisting of only Sn₄Ni₃ phase and 80 mass% of graphite were mixed sufficiently in a mortar to prepare the negative active material. A paste was mixed and prepared so as to consist of 50 mass% of this negative active material, 5 mass% of PVdF and 45 mass% of NMP, and applied to both surfaces of Cu foil of 27 mm in width and 10 μm in thickness; the coated foil was

dried at 150 °C to evaporate NMP and then pressed to adjust the porosity; and thus the negative electrode was provided. Except for using this negative electrode, two pieces each of Battery (Y12) of Comparative Example 11 were manufactured in an identical manner to

5   that of Embodiment 19.

In the battery of Comparative Example 10, a mixture of a material consisting of Sn phase alone and graphite was used as the negative active material. Except for using this negative active material, two pieces of Battery (Y13) of Comparative Example 10 were

10   manufactured in an identical manner to that of Comparative Example 9.

In the battery of Embodiment 261, the same alloy as the one used in Embodiment 26 was used and no graphite was mixed; except for the above, the battery was manufactured in an identical manner to that

15   of Embodiment 26.

The details of the batteries manufactured above, Embodiments 26 and 261 and Comparative Examples 8 to 10 were summarized in Table 9 and Table 10. Here, the values of the contents are expressed by the figures which were rounded to the nearest integer, the alloy

20   contains only Sn or Ni, and confirmation that only Sn phase or Sn_4Ni_3 phase are contained has been made.

(Table 9)

	Battery code	Element content in alloy mass%		Porosity %	Composition of negative active material mass%			Alloy X	
		Sn	Ni		Graphite	Sn_4Ni_3 phase	Sn phase	Z value	S value
Embodiment 26	Y10	86	14	33	80	10.5	9.5	1.1	0.25
Comparative Example 8	Y11			33	100	0	0	-	0.25
Comparative Example 9	Y12	73	27	33	80	20	0	-	0.25
Comparative Example 10	Y13	100		33	80	0	20	0	0
Embodiment 261	Y101	86	14	33	0	52.5	47.5	1.1	-

(Table 10)

	Battery code	Mass per one side surface of composite layer mg/cm²	
		Negative electrode	Positive electrode
Embodiment 26	Y10	8.35	21.62
Comparative Example 8	Y11	10.09	21.27
Comparative Example 9	Y12	10.75	20.99
Comparative Example 10	Y13	7.31	22.55
Embodiment 261	Y101	11.85	23.63

Concerning Batteries (Y10) to (Y13) of Embodiments 26 and 261 and Comparative Examples of 8 to 10, battery swelling, the discharge capacity at the 1st cycle, capacity density and the capacity retention at

5   the 50th cycle were determined under the same conditions as Battery (Y1) of Embodiment 19. The results were summarized in Table 11.

(Table 11)

	Battery code	Battery swelling mm	Discharge capacity at the 1st cycle mAh	Capacity density mAh/cm³	Capacity retention at the 50th cycle %
Embodiment 26	Y10	0.10	695	122	95.2
Comparative Example 8	Y11	0.38	695	122	89.9
Comparative Example 9	Y12	0.33	692	121	93.8
Comparative Example 10	Y13	1.12	694	121	71.1
Embodiment 261	Y101	0.61	693	121	92.8

Based on the results in Table 11, the following were revealed. Compared to Battery (Y10) of Embodiment 26, where alloy X and

10   graphite were contained in the negative active material, Battery (Y11) of Comparative Example 8, where only graphite was used as the negative active material, exhibited an increase in battery swelling and a decrease in capacity retention. In addition, in Battery (Y12) of Comparative Example 9, where Sn_4Ni_3 phase and graphite were

15   contained in the negative active material, battery swelling was large. Moreover, in Battery (Y13) of Comparative Example 10, where Sn phase and graphite were contained in the negative active material, battery swelling was significantly large and the capacity retention at the 50th

cycle was significantly low. Furthermore, in Comparative Examples 8 and 9, it was noted that metallic lithium deposition occurred and caused the swelling of the batteries. In addition, in Comparative Examples 8 and 9 compared to other batteries, more active materials

5   were put in so that the discharge capacities of these batteries were conformed to those of other batteries; hence, this contributes to an increase in swelling, too. The reason for putting in many active materials is that Sn_4Ni_3 phase has little capability of charge/discharge and that the charge/discharge capacity of graphite is

10   remarkably low compared to that of Sn phase.

From the above described findings, in order to reduce battery swelling in the fast charge process at a low temperature and to enhance cycle life performance, it was found to be preferable that the negative electrode contain the alloy which contains Sn_4Ni_3 phase and Sn phase

15   and carbon material.

When the negative active material contains the alloy X which contains Sn_4Ni_3 phase and Sn phase and carbon material, volumetric capacity is large compared to that of carbon material, because the negative active material contains Sn phase superior in Li^+ storage

20   ability compared to the case where only carbon material is contained. Alloy X contains Sn_4Ni_3 phase inferior in insertion/extraction of Li, and this serves as a framework structure of preventing the volume expansion/contraction or crack from occurring at the time of Li^+ insertion/extraction in the alloy material; therefore, it is believed that

25   the battery of the present invention exhibited the equal or higher capacity density and cycle life performance than those of conventional type, at room temperature.

Embodiments 27 to 31 and Embodiments 11c and 12c

In these examples, Z values of alloy X to be used as the negative

30   active material were set to be 1.1, and the mixture ratios of alloy X and carbon material, S values (= n_1/n_2), were varied; except for the above, two pieces each of Batteries (Y14) to (Y20) of Embodiments 27 to 31 and Embodiments 11c and 12c were manufactured in an identical manner to that of Embodiment 19. The details of the batteries manufactured

35   above were summarized in Table 12. In addition, the battery of Embodiment 26 was also listed in Table 12.

(Table 12)

| | Battery code | S value of negative active material | Mass per one side surface of composite layer mg/cm^2 | |
			Negative electrode	Positive electrode
Embodiment 11c	Y19	0.03	8.48	21.64
Embodiment 27	Y14	0.05	8.47	21.32
Embodiment 28	Y15	0.07	8.42	21.43
Embodiment 26	Y10	0.25	8.35	21.62
Embodiment 29	Y16	0.50	8.17	21.86
Embodiment 30	Y17	1.00	7.74	21.96
Embodiment 31	Y18	3.5	7.21	22.06
Embodiment 12c	Y20	4.0	6.92	22.36

Concerning Batteries (Y14) to (Y20) of Embodiments 27 to 31 and Embodiments 11c and 12c, battery swelling, the discharge capacity at the 1st cycle, capacity density and the capacity retention at the 50th cycle were determined under the same conditions as Battery (Y1) of Embodiment 19. The results were summarized in Table 13.

(Table 13)

	Battery code	Battery swelling mm	Discharge capacity at the 1st cycle mAh	Capacity density mAh/cm^3	Capacity retention at the 50th cycle %
Embodiment 11c	Y19	0.27	696	122	90.3
Embodiment 27	Y14	0.14	693	122	94.3
Embodiment 28	Y15	0.12	697	121	94.8
Embodiment 26	Y10	0.10	695	122	95.2
Embodiment 29	Y16	0.11	695	122	95.2
Embodiment 30	Y17	0.12	693	121	94.3
Embodiment 31	Y18	0.14	693	121	92.5
Embodiment 12c	Y20	0.30	694	121	89.5

In addition, Fig. 7 shows the relationship between the S value, which is the ratio of the mass of alloy X (n_1) to the mass of carbon material (n_2) in the negative electrode, and battery swelling in these

batteries.

Table 13 and Fig. 7 revealed the following. In Batteries (Y10) and (Y14) to (Y18) of Embodiments 26 to 31, where S value of the negative active material falls within the range of 0.05 to 3.5, battery swelling was small, not greater than 0.14 mm, and capacity retention at the 50th cycle was high. While, in Battery (Y19) of Embodiment 11c, where S value is 0.03, and Battery (Y20) of Embodiment 12c, where S value is 0.30, battery swelling was not less than 0.25 mm, and capacity retention at the 50th cycle was low.

The reason for this is inferred as follows: in case of S<0.05, the ratio of the mass of alloy X to that of carbon material was significantly low, so that the effect of reducing metallic lithium production in the fast charge process at a low temperature was insufficient and this resulted in battery swelling.

It is also inferred that in case of S>3.5, the ratio of the mass of alloy X to that of carbon material was high, so that the effect of expansion of alloy X became large, current collection performance in the negative electrode plate deteriorated and current distribution became nonuniform; as a result, Li storage reaction in carbon material as well as metallic lithium production reaction occurred and this resulted in battery swelling.

Embodiment 32

In this example, Sn powder, Ni powder and Ag powder were weighed out to 88 mass%, 9 mass% and 3 mass%, respectively, and preparatively mixed in a mortar. This mixed powder was press molded into pellet form, and then placed on a water cooled copper hearth in an arc melting furnace. After the furnace atmosphere was substituted with Ar atmosphere, the pellet was melted by the irradiation of arc discharge, which was stopped after the molten metal was observed to have been mixed sufficiently. The molten metal was cooled by the water cooled copper hearth and formed a button-like solid. The cooling rate of the molten metal on the water cooled copper hearth was 5×10^2 °C /sec. The obtained button-like solid was polished until the surface had a metallic luster, the polished one was then ground, and thus alloy Y was obtained.

From the X-ray diffraction pattern (X-ray source: CuKa, and

measurement range: $28° \leq 2\theta \leq 42°$) shown in Fig. 8, it was noted that this alloy Y contained only Sn phase, Sn_4Ni_3 phase and Ag_3Sn phase. The quantitative analysis of element was conducted for this alloy Y using ICP emission spectrometry. Supposing that the masses of Sn, Ni

5   and Ag elements are defined to be p mass%, q mass% and r mass%, respectively, and that the masses of Sn phase, Sn_4Ni_3 phase and Ag_3Sn phase in alloy Y are defined to be v mass%, w mass% and u mass%, respectively. This alloy Y consists of only Sn phase, Sn_4Ni_3 phase and Ag_3Sn phase; hence the following relational expressions are formulated

10   between them.

   p = [mass of Sn phase] + [mass of Sn in Sn_4Ni_3 phase] +
        [mass of Sn in Ag_3Sn phase]
     = v + w × [formula mass of Sn] / [formula mass of Sn_4Ni_3] +
        u × [formula mass of Sn] / [formula mass of Ag_3Sn]

15   = v + w × 474.8 / 650.9 + u × 118.7 / 442.3
   q = w × [mass of Ni in Sn_4Ni_3 phase]
     = w × [formula mass of Ni] / [formula mass of Sn_4Ni_3]
     = w × 176.1 / 650.9
   r = w × [mass of Sn in Ag_3Sn phase]

20   = w × [formula mass of Ag] / [formula mass of Ag_3Sn]
     = w × 323.6 / 442.3

   Using the p, q and r values obtained by the quantitative analysis of element, the above described relational expressions were solved simultaneously to determine the values of v, w and u.

25   Furthermore, using these values, Z (= v/w) value was accordingly found to be 1.9. Except for using this powder, Battery (Y21) of Embodiment 32 was manufactured in an identical manner to that of Embodiment 19 (S = 0.25). Battery swelling, the discharge capacity at the 1st cycle, capacity density and the capacity retention at the 50th cycle were

30   determined under the same conditions as Embodiment 19. The results were obtained as follows:

   Mass per one side surface of negative composite layer =
        8.45 mg/cm^2

   Mass per one side surface of composite layer =21.58 mg/cm^2

35   Battery swelling = 0.15 mm

   Discharge capacity at the 1st cycle = 695 mAh

Capacity density = 122 mAh/cm³

Capacity retention at the 50th cycle = 95.7 %.

In alloy Y used in the negative electrode of Battery (Y21) of Embodiment 31, Ag_3Sn phase is present in addition to Sn phase and

5　Sn₄Ni₃ phase. This indicates that it is possible to contain a phase other than Sn phase and Sn_4Ni_3 phase in alloy X to be used in the negative electrode of the non-aqueous electrolyte battery of the present invention. It is preferable that a phase other than Sn phase and Sn_4Ni_3 phase be not greater than 50 mass% with respect to total mass of alloy

10　Y. This is due to the reason that the effects based on the above described mechanisms, such as the increase in discharge capacity and the prevention of volume expansion/contraction or crack occurrence, become less.

Measurement of alloy grinding time

15　Alloy X used in Batteries (Y1) to (Y10) was ground by ball milling method, and the time required for the particle size at 90 % of mass integration, D_{90}, to reach 45 μm and smaller was measured and termed as preparation time. The results are shown in Table 14.

(Table 14)

	Battery code	Alloy X	
		Z value	Preparation time　hr.
Comparative Example 6	Y8	0.1	90
Embodiment 19	Y1	0.2	28
Embodiment 20	Y2	0.3	18
Embodiment 21	Y3	0.5	16
Embodiment 26	Y10	1.1	12
Embodiment 22	Y4	1.2	12
Embodiment 23	Y5	1.5	14
Embodiment 24	Y6	2.0	16
Embodiment 25	Y7	3.0	18
Embodiment 7c	Y9	4.5	20

20　From Table 14, the time required to grind material X used in Batteries (Y1) to (Y7), (Y9) and (Y10) of Embodiments 19 to 26 and

Embodiment 7c was found to be significantly short compared to that for grinding material X used in Battery (Y8) of Comparative Example 6.

Based on the above findings, it was revealed that when the mass ratio of Sn_4Ni_3 phase to Sn phase in material X was not less than 0.2, the time for preparing negative electrode was able to be reduced.

INDUSTRIAL APPLICABILITY

The present invention enables practical application of a non-aqueous electrolyte secondary battery which has high energy density and satisfactory cycle performance.